# THERMAL EXPANSION OF THE SKUTTERUDITE SUPERCONDUCTOR $PrOs_4Sb_{12}$*

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*(Received July 10, 2002)*

The recently discovered Pr-based skutterudite superconductor $PrOs_4Sb_{12}$ was studied by means of low-temperature measurements of the thermal expansion coefficient $\alpha$ along the cubic (100) direction of a single crystal sample in magnetic fields up to 8 T. Two superconducting phase transitions were found with critical temperatures $T_{c1} = 1.84$ K and $T_{c2} = 1.71$ K. Their hydrostatic pressure dependencies calculated using the Ehrenfest relation are $-250 \pm 50$ mK/GPa and $-450 \pm 70$ mK/GPa, respectively. For $B \geq 5$ T, we observe a thermodynamic phase transition which is presumably due to the onset of quadrupolar order. The transition temperature shifts with increasing $B$ towards higher temperatures. The strongly enhanced value of the Grüneisen parameter $\Gamma$ provides clear evidence for the occurrence of a heavy-fermion normal state. The pronounced change of $\Gamma$ at $T_c$ provides evidence for the formation of Cooper pairs out of the heavy quasiparticles.

PACS numbers: 71.27.+a, 74.70.Tx, 75.30.Mb, 74.25.Dw

A large variety of different ground states have been found in the class of filled skutterudite compounds $MT_4X_{12}$ (M = lanthanide or actinide metal, T = Fe, Ru, Os, X = P, As, Sb); *e.g.*, superconductivity ($LaFe_4P_{12}$, $LaRu_4Sb_{12}$), Kondo insulator ($CeFe_4P_{12}$, $UFe_4P_{12}$), heavy-fermion ($CeFe_4Sb_{12}$, $YbFe_4Sb_{12}$), and non-Fermi liquid ($CeRu_4Sb_{12}$) behaviour [1]. They crystallize in the cubic $LaFe_4P_{12}$ structure with $TX_3$ cages filled by lanthanide or actinide atoms [2].

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

A new member of the class of filled skutterudites, $PrOs_4Sb_{12}$, exhibits heavy-fermion behaviour and superconductivity and is considered to be the first Pr-based heavy-fermion superconductor [3]. The susceptibility data are best described by a crystalline-electric field scheme with a non-magnetic $\Gamma_3$ ground state which causes an electric quadrupole moment separated from a $\Gamma_5$ triplet [1]. The large size of the jump in the specific heat at $T_c \sim 1.8\,$K, $\Delta C/T_c$, which is of the same order of magnitude as the Sommerfeld coefficient $\gamma_0$ suggests heavy-fermion superconductivity in $PrOs_4Sb_{12}$ [3].

Here we report on ultrahigh resolution thermal expansion measurements on single crystal $PrOs_4Sb_{12}$ down to 50 mK and in fields up to 8 T. The linear thermal expansion coefficient $\alpha$ is defined as $\alpha = l^{-1}\,\partial l/\partial T$ where $l$ denotes the sample length. For a cubic system, the volume thermal expansion coefficient $\beta(T)$ is given by $3\,\alpha(T)$. Two samples were mounted on top of each other to improve the resolution. The upper part of Fig. 1 shows the volume thermal expansion coefficient $\beta$ *vs* $T$. Two superconducting phase

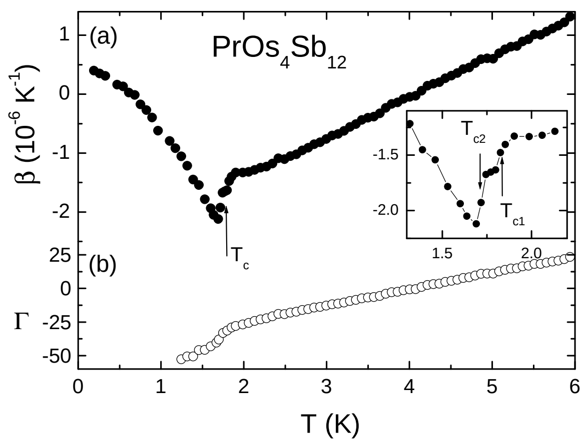


Fig. 1. (a) $T$ dependence of the volume thermal expansion coefficient $\beta$ (a) and Grüneisen parameter $\Gamma$; (b) for $PrOs_4Sb_{12}$. The arrows mark the superconducting phase transitions in $\beta$ *vs* $T$ enlarged in the inset.

transitions lying close to each other separated by a small plateau are resolved with transition temperatures $T_{c1} = 1.84\,$K and $T_{c2} = 1.71\,$K (*cf.* inset of Fig. 1). This might be caused by different transitiontemperatures of both crystals. However, specific heat measurements on one sample also showed two transitions with similar $T_c$ values [1]. Further arguments in favor of two transitions are given by the calculation of the hydrostatic pressure dependence of $T_c$ by using the Ehrenfest relation, $\partial T_c/\partial p = V_{mol}\,T_c\,\Delta\beta/\Delta C$. Here $V_{mol} = 2.42 \times 10^{-4}\,m^3/mol$ and $\Delta C$ denote the molar volume and the jump height of $C$ at $T_c$, respectively. $\Delta\beta(T_c)$ is estimated by an equal-areas construction. For the transition temperature $T_{c1}$ we deduce a hydrostatic pressure dependence of $-250\pm 50$ mK/GPa, which is slightly higher than the value obtained by resistivity measurements under hydrostatic pressure [1]. The pressure dependence of $T_{c2}$ is found to be $-450\pm 70$ mK/GPa. Assuming only one transition in $\beta$ and $C$ a value of $-510\pm 100$ mK/GPa would be derived which is three times higher than that of the resistivity measurements under hydrostatic pressure. Thus, the splitting of the transition seems to be intrinsic, although its origin is still unknown. The occurrence of two transitions could hint to unconventional superconductivity with a multicomponent order parameter as found for $UPt_3$ [4].

In the lower plot of Fig. 1 the Grüneisen parameter $\Gamma$ *vs* $T$ for $PrOs_4Sb_{12}$ is shown. The Grüneisen parameter is defined by $\Gamma = V_{\rm mol}/\kappa_T\, \beta/C$, where the value $4.7\times 10^{-12}$ Pa for the isothermal compressibility $\kappa_T$ for $PrFe_4P_{12}$ was used [5]. The corresponding specific heat data are taken from [3]. The Grüneisen parameter for $PrOs_4Sb_{12}$ at $T = 6$ K exceeds the typical values for ordinary metals ($\Gamma\sim 1$) by a factor of 10 and decreases linearly upon lowering $T$. The highly enhanced Grüneisen parameter in the normal state provides strong evidence that $PrOs_4Sb_{12}$ forms a heavy-fermion state at low temperatures. The strong change of the Grüneisen parameter at $T_c$ gives clear evidence for the occurrence of heavy-fermion superconductivity formed by the heavy quasiparticles.

The magnetic field dependence of the linear thermal expansion coefficient $\alpha$ is shown in Fig. 2. For $B > 1$ T, the superconducting jump is not resolvable anymore although the upper critical field is found to be 2.2 T [3]. The minimum structure in $\alpha$ whose minimum temperature $T_{\rm min}$ shifts to-

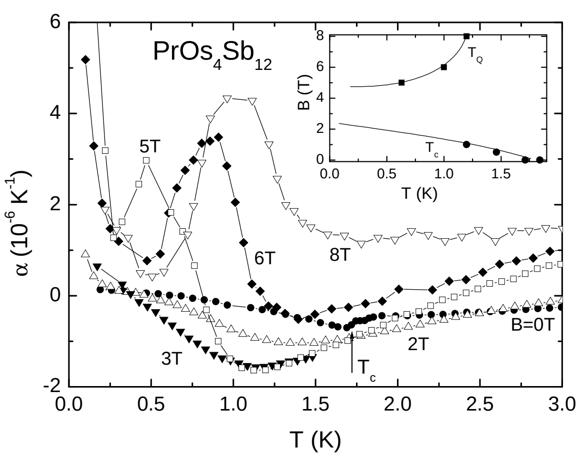


Fig. 2. Linear thermal expansion coefficient $\alpha$ *vs* $T$ in different fields $B\leq 8$ T. Inset: $B$-$T$ diagram with superconducting ($T_c$), and, presumably, quadrupolar ordering ($T_Q$) phase transitions. Lines are guides to the eye.

wards lower temperatures upon increasing the field to 5 T corresponds to the Schottky anomaly found in specific heat. The feature can also be fitted by a Schottky term with an additional term taking into account the $T$ dependence of the Grüneisen parameter. The low $T$ up-turns are caused by the hyperfine splitting of the Pr nucleus.

Upon increasing the magnetic field to $B \geq 5\,\mathrm{T}$, a second phase transition occurs. The transition temperature $T_Q$ and the jump height in $\alpha(T)$ increase upon increasing the field. The resulting $B$-$T$ phase diagram is shown in the Inset of Fig 2. The high field transition at $T_Q$ is presumed to be a transition into quadrupolar ordering. A similar field dependence of the phase-transition line was found for $PrPb_3$ which is known to exhibit quadrupolar order [6].

To summarize, we confirmed the occurrence of heavy-fermion superconductivity in $PrOs_4Sb_{12}$ by an analysis of the low-temperature thermal expansion and Grüneisen parameter. Two superconducting phase transitions were found in thermal expansion and specific heat measurements. This points to unconventional superconductivity in $PrOs_4Sb_{12}$. For $B \geq 5\,\mathrm{T}$, the quadrupolar moments presumably order at $T_Q$.

The research at UCSD was supported by the US DOE and NSF.

## REFERENCES

[1] M.B. Maple, P.-C. Ho, V.S. Zapf, N.A. Frederick, E.D. Bauer, W. Yuhasz, F.M. Woodward, J.W. Lynn, *J. Phys. Soc. Jpn.* **71** Suppl., 23 (2002).

[2] W. Jeitschko, D.J. Braun, *Acta Crystallogr.* **B 33**, 3401 (1977).

[3] E.D. Bauer, N.A. Frederick, P.-C. Ho, V.S. Zapf, M.B. Maple, *Phys. Rev.* **B65**, 100506(R) (2002).

[4] R. Fisher, S. Kim, B.F. Woodfield, N.E. Phillips, L. Taillefer, K. Hasselbach, J. Flouquet, A.L. Giorgi, J.L. Smith, *Phys. Rev. Lett.* **62**, 1411 (1989).

[5] Y. Nakanishi, T. Simizu, M. Yoshizawa, *Phys. Rev.* **B63**, 184429 (2001).

[6] T. Tayama, T. Sakakibara, K. Kitami, M. Yokoyama, K. Tenya, H. Amitsuka, D. Aoki, Y. Onuki, Z. Kletowski, *J. Phys. Soc. Jpn.* **70**, 248 (2001).